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Europäisches Patentamt
European Patent Office
Office européen des brevets

19

11 Publication number:

0 022 336
A1

12

EUROPEAN PATENT APPLICATION

21 Application number: 80302164.1

22 Date of filing: 27.06.80

51 Int. Cl.³: C 08 G 18/18
C 08 G 18/50, C 08 L 71/02
C 08 K 5/20, C 08 K 5/17
C 08 K 5/10

30 Priority: 29.06.79 US 53441

43 Date of publication of application:
14.01.81 Bulletin 81/2

84 Designated Contracting States:
DE FR GB IT NL

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54 Premix compositions for use in the production of flame retardant polyurethane foams.

57 The storage stability of otherwise unstable premix compositions for flame retardant polyurethane foams containing in the premix a halogenated polyol and a tertiary amine catalyst can be enhanced by incorporating into the premix a condensation product of acrylic or methacrylic acid with an alcohol or an amine.

EP 0 022 336 A1

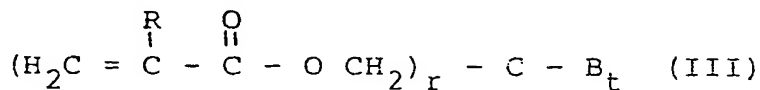
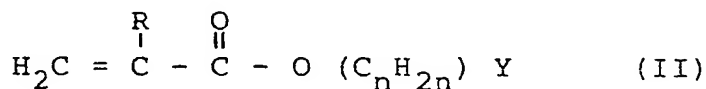
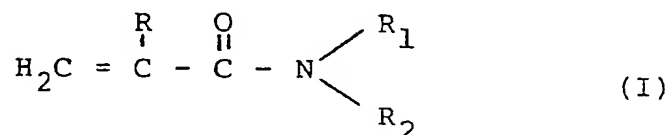
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This invention relates to premix compositions for use in the production of flame retardant rigid polyurethane foams and is particularly concerned with improving the storage stability of such premix compositions.

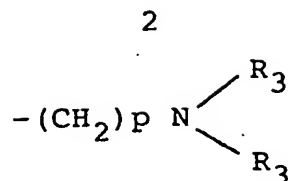
Premix compositions for rigid flame retardant polyurethane foams containing halogenated polyols are unstable at room or elevated temperature when such premix compositions contain a tertiary amine catalyst. Apparently decomposition of the halogenated polyol gives rise to HX which forms a tertiary amine hydrohalide salt and deactivates the catalyst.

We have now found that the stability of such premix compositions can be enhanced by inclusion therein of a condensation product of acrylic or methacrylic acid with an alcohol or amine.

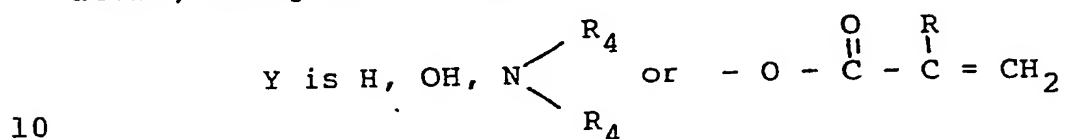
Among the esters and amides of acrylic and methacrylic acid found particularly beneficial are those corresponding to the formulae:



wherein R is H or CH₃; R₁ is H, an alkyl radical of 1 to 4 carbon atoms, or a hydroxyalkyl radical of 2 to 3 carbon atoms; R₂ is an alkyl radical of 1 to 4 carbon atoms, a hydroxy alkyl radical of 2 to 3 carbon atoms, or a substituted amino alkyl group of the formula



5 wherein each R_3 is independently an alkyl radical of 1 to 4 carbon atoms or a hydrogen alkyl radical of 2 to 3 carbon atoms, and p is 2 to 4;



15 wherein each R_4 is independently an alkyl radical of 1 to 4 carbon atoms and n is 1 to 12, provided that n is 2 when Y is OH or $\text{N} \begin{array}{l} \nearrow \text{R}_4 \\ \searrow \text{R}_4 \end{array}$; and

B is hydrogen or an alkyl radical of 2 to 4 carbon atoms, r is 3 or 4, t being zero when r is 4 and t being 1 when r is 3.

20 Particularly preferred condensation products comprise dimethylamino ethyl acrylate, dimethylamino ethyl methacrylate, isobutyl methacrylate, and mixtures thereof.

Advantageously the tertiary amine catalyst is dimethylethanolamine.

25 Typically, the premix composition will also include a blowing agent and a surfactant cell stabilizer. The blowing agent typically comprises a chlorofluorocarbon and the cell stabilizer is typically a siloxane compound.

30 In use, the required di- or poly- isocyanate is added to the premix composition to initiate the isocyanate-polyol reaction and blowing to produce the desired rigid flame retardant cellular polyurethane.

35 The premix composition may contain any of the known tertiary amine catalysts employed in the production of rigid cellular polyurethanes or mixtures of such catalysts. Particular examples of these include triethylene diamine, dimethyl ethanolamine, dimethyl cyclohexylamine, triethylam-

ine, N-methyl morpholine, dimethyl piperazine, tetramethyl propane diamine. More frequently employed are the aliphatic tertiary amines, particularly dimethylethanolamine.

5 The surfactant employed as a cell stabilizer may be of the silicone oil type such as polysiloxane-polyoxyalkylene block copolymers or polydimethyl siloxane; or the type obtained by polymerization of dibutyl maleate monomer and an N-vinyl pyrrolidone monomer compound in a polyol polymerization medium (U.S. Patent No. 3,746,663).

10 Any of the usual blowing agents generally employed in rigid polyurethane formulations may be employed, preferably those of the halohydrocarbon type, such as trichlorofluoromethane.

15 The halogenated polyol may be a halogenated aliphatic or cycloaliphatic polyester or polyether polyol or mixtures thereof having 2 to 8 hydroxyl groups, there being at least one chlorine or bromine atom attached to a carbon of the polyol. Typical chlorinated polyols more frequently employed in flame retardant polyurethanes are the chlorinated poly-
20 ether polyols having hydroxyl number values of from about 200 to about 700 and having a chlorine content in the range of about 25 to 60% by weight. Particularly preferred is a chlorinated polyether polyol having a hydroxyl number of 365 ± 10 and containing about 47% by weight of chemically bound
25 chlorine.

A particularly preferred premix composition comprises, by weight

halogenated polyether polyol	100
chlorofluorocarbon blowing agent	45
dimethylethanolamine	3.5
condensation product	2 to 4

30

To such premix composition may be added 20 parts, by weight, of an amino polyol for reducing surface friability of polyurethane foam, said amino polyol having a hydroxyl number of 600 ± 10 and a viscosity of 280 cps at 25°C, and optionally
35 a cell stabilizing siloxane compound.

EXAMPLE 1

A series of experimental runs were made to determine the effectiveness of the condensation product in retarding deactivation of the catalyst in the premix for fire retardant rigid polyurethane foams. In all of these runs the same basic premix composition was employed. The basic premix composition comprised:

		<u>pbw</u>
10	Thermolin TM RF-230 (1)	100
	Poly G ^R , 70-600 (2)	20
	Genetron ^R , R11SBA (3)	45
	Cell stabilizer (4)	1.5
	Tertiary amine catalyst	(as indicated)
15	Condensation product	(as indicated)

(1) A reactive chlorinated polyether polyol supplied by Olin Corporation Designed Products Division for use in production of flame retardant rigid polyurethanes. The product contains 47% by weight chemically bound chlorine and has a hydroxyl number of 365 ± 10 (mg KOH/gm) and a viscosity of 100,000 cps at 25°C.

(2) An amino-polyol supplied by the above-named Olin Division specifically designed to reduce surface friability in rigid polyurethane foams based on Thermolin RF230. It has a hydroxyl number of 600 ± 10 (mg KOH/gm) and a viscosity of 280 cps at 25°C.

(3) Trichloro monofluoromethane blowing agent.

(4) LK-221TM or DC-193 copolymers were employed. LK-221 copolymer, supplied by Air Products and Chemicals, Inc., is a copolymer of N-vinyl pyrrolidone and dibutyl maleate polymerized in a trifunctional polyol. DC-193, supplied by Dow-Corning comprises polysiloxane-polyoxyalkylene block copolymers as described in US Patents 2,834,748 and 2,917,480.

Before and after storage of the foregoing premix composition at about 38-41°C for indicated time periods, the activity was determined by reaction with Mondur^R MR⁵.

5 (5) A polymethylene polyphenol isocyanate supplied by Mobay Chemical Co., containing 32% NCO groups, having an equivalent weight of 132.

10 The results are reported in Tables 1 and 2 comparing the stabilized premix compositions with an unstabilized premix composition, each employing dimethyl ethanol amine (DMEA) catalyst (3.5 parts catalyst in stabilized compositions and 3.7 parts in the control).

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TABLE 1

Condensation Product (Stabilizer)	NONE	n-Lauryl Methacrylate 3.0			Dimethyl amino ethyl acrylate 2.0			Trimethylol propane triacrylate 2.0			Triethylene glycol diacrylate 2.0			Hydroxyethyl methacrylate 3.0			Hydroxyethyl methacrylate 4.0				
		a	e	f	a	b	c	a	b	c	a	b	c	a	b	d	a	b	d		
		pbv																			
Cream time (secs.)	9	11	16	11	13	13	11	11	11	13	13	12	13	14	12	13	13	12	13	14	
Gel time (secs.)	31	26	49	34	37	38	30	29	30	34	36	38	34	37	39	34	37	37	33	38	40
Tack-free time (secs.)	43	49	71	39	47	45	34	33	32	41	42	48	37	42	46	37	43	47	39	42	45
Rise time (secs.)	59	71	90	78	60	68	63	65	68	78	78	86	72	81	80	75	76	79	73	75	80
Percent loss																					
Cream time	-	22	78	-	18	18	-	0	0	-	18	18	-	8	17	-	8	8	-	8	17
Gel time	-	16	58	-	9	12	-	0	0	-	6	12	-	9	15	-	8	8	-	15	21
Tack-free time	-	17	65	-	21	15	-	0	0	-	2	17	-	14	24	-	16	27	-	8	15
Rise time	-	20	73	-	0	0	-	3	8	-	0	10	-	13	11	-	1	5	-	3	10

a) Initial
b) after 11 days
c) after 19 days
d) after 18 days
e) after 8 days
f) after 15 days
g) after 12 days

TABLE 2

TABLE 2

Condensation Product (Stabilizer) pbw	Isobutyl Methacrylate												Isobutyl Methacrylate												1,3-Butylene dimethacrylate																							
	None												3.0												4.0												2.0											
	a	e	f	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d												
Cream time (secs.)	9	11	16	13	13	14	13	13	14	13	13	14	12	13	14	12	13	12																														
Gel time (secs.)	31	26	49	34	37	37	34	37	36	33	35	37																																				
Tack-free time (secs.)	43	49	71	40	44	46	39	43	45	37	43	45																																				
Rise time (secs.)	59	71	90	75	82	81	78	71	79	79	75	75																																				
Percent loss																																																
Cream time	-	22	78	-	0	8	-	0	8	-	8	0	-	8	0	-	8	0																														
Gel time	-	16	58	-	9	9	-	9	6	-	6	12																																				
Tack-free time	-	17	65	-	10	15	-	10	15	-	16	22																																				
Rise time	-	20	73	-	9	8	-	0	1	-	0	0																																				

a) initial
b) after 11 days
c) after 19 days
d) after 18 days
e) after 8 days
f) after 15 days
g) after 12 days

TABLE 2 (Continued)

Condensation Product (Stabilizer) pbw	Trimethylol propane trimethac- rylate 2.0			1,6-Hexane diol diacrylate 2.0			Dimethylamino- propyl meth- acrylamide 2.0			Dimethylamino- ethyl methac- rylate 2.0			Isobutyl methacry- lamide 3.0		
	a	b	d	a	b	d	a	b	d	a	b	d	a	b	d
Cream time (secs.)	12	13	13	12	13	14	11	12	12	11	11	12	13	13	14
Gel time (secs.)	33	35	37	34	36	38	27	29	29	28	30	30	34	36	38
Tack-free time (secs.)	37	44	40	37	44	43	30	34	36	34	35	33	39	43	44
Rise time (secs.)	74	71	71	73	78	76	56	58	57	65	60	62	65	74	75
Percent loss Cream time	8	8	8	-	8	17	-	9	9	-	0	9	-	0	8
Gel time	-	6	12	-	6	12	-	7	7	-	7	7	-	6	12
Tack-free time	-	19	8	-	19	16	-	13	20	-	3	0	-	10	13
Rinse time	-	0	0	-	7	4	-	4	2	-	0	0	-	14	15

a) initial
b) after 11 days
c) after 19 days
d) after 18 days
e) after 8 days
f) after 15 days
g) after 12 days

The low activity losses indicate that the premix compositions stabilized with the condensation products of Tables 1 and 2 can be successfully used after storage at ambient temperature for prolonged periods of up to about six months.

5 In addition to the condensation products disclosed in Tables 1 and 2, other examples of compounds corresponding to Formula (I) include:

10 bishydroxyethylacrylamide
 dibutyl acrylamide
 diethyl acrylamide

Examples of compounds corresponding to Formula (II) in addition to those specifically named in the Tables above, are:

15 hydroxyethyl acrylate
 hydroxyethyl methacrylate

An example of a compound corresponding to Formula
20 (III) in which $r = 4$, is

pentaerythritol tetraacrylate

25 The rapid loss in activity (over 50% loss) shown by the unstabilized control is a common occurrence not only with the DMEA catalyst used in the reported test but also is found with other tertiary amine catalysts when employed in premix compositions containing halogenated polyols. The condensation products of the present invention are effective in
30 retarding the rate of loss in activity of fire retardant polyurethane premix compositions employing such other tertiary amine catalysts.

Results of stability tests made on flame retardant polyurethane premix compositions with other tertiary amine
35 catalysts are reported in Tables 3 and 4.

TABLE 3

STABILIZER (pbw)	CATALYST (pbw)	NONE	DMAEM 1.0				DMAEM 3.0				DMAEM 1.0			
			DMEA 3.5				DMEA 3.5				(a) 2.5			
		A C E	A	B	D	A	B	D	A	B	A	B	D	
Cream time (secs.)		9 11 16	10	11	13	10	10	10	10	10	11	13	14	
Gel time (secs.)	31	26 49	32	34	34	30	29	30	30	29	30	34	38	
Tack-free time (secs.)	43	49 71	38	38	43	34	32	37	36	32	36	42	47	
Rise time (secs.)	59	71 90	72	74	75	61	68	65	64	68	64	73	77	
Percent loss														
Cream time		- 22 78	-	10	30	-	0	0	-	0	-	18	27	
Gel time		- 16 58	-	6	6	-	0	0	-	0	-	13	27	
Tack-free		- 18 65	-	0	13	-	0	9	-	0	-	17	31	
Rise time		- 20 73	-	3	4	-	11	17	-	11	-	14	20	

A = initial

B = after 7 days

C = after 8 days

D = after 14 days

E = after 15 days

DMAEM = dimethylaminoethyl methacrylate

DMEA = dimethyl ethanolamine

(a) = 20% triethylene diamine - 80% dimethylethanolamine

(b) = 33% triethylene diamine - 67% dipropylene glycol

TABLE 3 (Continued)

STABILIZER (pbw)	DMAEM 5.0				DMAEM 1.0				DMAEM 3.0				DMAEM 5.0			
	(a)	(b)	(b)	(b)	(a)	(b)	(b)	(b)	(a)	(b)	(b)	(b)	(a)	(b)	(b)	(b)
CATALYST (pbw)	2.5	3.5	3.5	3.5	2.5	3.5	3.5	3.5	2.5	3.5	3.5	3.5	2.5	3.5	3.5	3.5
	A	B	D	A	B	D	A	B	D	A	B	D	A	B	D	D
Cream time (secs.)	10	10	13	13	13	14	18	13	14	14	14	14	12	12	13	13
Gel time (secs.)	27	27	29	33	36	43		28	32	35			27	28	30	30
Tack-free time (secs.)	31	33	33	39	45	50		35	37	43			33	34	37	37
Rise time (secs.)	53	61	55	60	70	77		65	62	66			48	55	62	62
Percent loss																
Cream time	-	0	30	-	8	38		-	8	8			-	0	8	8
Gel time	-	0	7	-	9	30		-	14	25			-	4	11	11
Tack-free	-	6	6	-	15	28		-	6	23			-	3	12	12
Rise time	-	15	4	-	19	28		-	13	20			-	15	29	29

A = initial

B = after 7 days

D = after 14 days

DMAEM = dimethylaminoethyl methacrylate

(a) = 20% triethylene diamine - 80% dimethylethanolamine

(b) = 33% triethylene diamine - 67% dipropylene glycol

TABLE 4

STABILIZER (pbw)	DMAEM		DMAEM		DMAEM		DMAEM		DMAEM		DMAEM	
	1.0	3.0	5.0	1.0	3.0	5.0	1.0	3.0	5.0	1.0	3.0	5.0
CATALYST (pbw)	(c)	(c)	(c)	(d)	(d)	(d)	(c)	(c)	(c)	(d)	(d)	(d)
	4.5	4.5	4.5	2.0	2.0	2.0	4.5	4.5	4.5	2.0	2.0	2.0
	A	B	D	A	B	D	A	B	D	A	B	D
Cream time (secs.)	13	13	13	12	12	12	12	12	10	10	10	9
Gel time (secs.)	37	36	36	34	33	39	30	29	28	24	26	23
Tack-free (secs.)	45	44	42	38	38	39	37	33	33	38	31	28
Rise time (secs.)	71	73	69	63	66	64	61	57	58	46	51	41
Percent loss	-	0	0	-	0	0	-	0	0	-	10	0
Cream time	-	0	0	-	0	0	-	0	0	-	8	21
Gel time	-	0	0	-	0	0	-	0	0	-	11	18
Tack-free	-	0	0	-	0	3	-	0	0	-	11	17
Rise time	-	3	0	-	5	2	-	0	0	-	11	17

(c) = dimethylaminoethyl morpholine

(d) = C-methyl triethylene diamine

In preparation of the activity-stabilized premix compositions of the invention only the usual amounts of tertiary amine catalyst need be employed as in the known formulations for rigid cellular polyurethane products. The total
5 amount of catalyst plus condensation product will in general comprise 5.5 to 7.5 parts per hundred parts of halogenated polyol in the premix composition.

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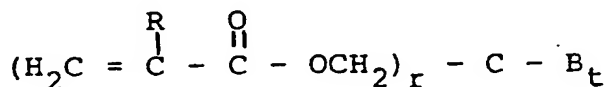
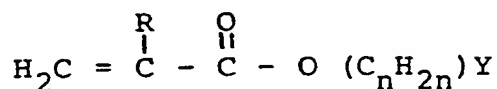
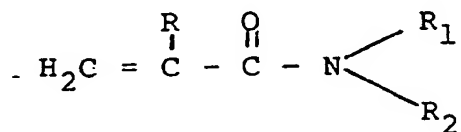
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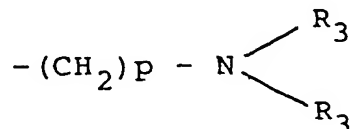
CLAIMS

1. A premix composition for use in the production of flame retardant polyurethane foams and comprising a tertiary amine catalyst and a halogenated polyol characterized in that
 5 said premix composition also contains a condensation product of acrylic or methacrylic acid with an alcohol or amine to enhance the storage stability of said premix composition.

2. A premix composition according to Claim 1, characterized in that said condensation product is of the formula from
 10 the group consisting of

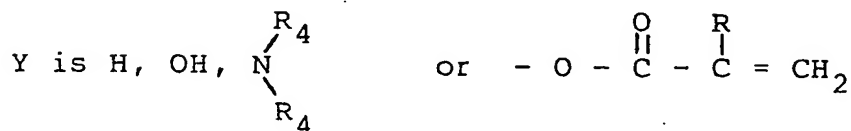


wherein R is H or CH₃; R₁ is H, an alkyl radical of 1 to 4 carbon atoms, a hydroxyalkyl radical of 2 to 3 carbon atoms;
 25 R₂ is an alkyl radical of 1 to 4 carbon atoms, a hydroxy alkyl radical of 2 to 3 carbon atoms; or a substituted amino alkyl group of the formula



wherein each R_3 is independently an alkyl radical of 1 to 4 carbon atoms, or a hydroxy alkyl radical of 2 to 3 carbon atoms, and p is 2 to 4

5



10 wherein each R_4 is independently an alkyl radical of 1 to 4 carbon atoms, and n is 1 to 12; provided that n is 2 when Y is OH or $N \begin{array}{c} \diagup R_4 \\ \diagdown R_4 \end{array}$; and

B is hydrogen or an alkyl radical of 2 to 4 carbon atoms, r is 15 3 to 4, t being zero when r is 4 and t being 1 when r is 3.

3. A premix composition according to Claim 1, characterized in that said condensation product is dimethylamino ethyl acrylate.

4. A premix composition according to Claim 1, characterized 20 in that said condensation product is dimethylamino ethyl methacrylate.

5. A premix composition according to Claim 1, characterized in that said condensation product is isobutyl methacrylate.

25 6. A premix composition according to any preceding Claim, characterized in that said tertiary amine catalyst is dimethylethanolamine.

7. A premix composition according to any preceding Claim, characterized in that said halogenated polyol is a chlorinated 30 polyether polyol having a hydroxyl number of 365 ± 10 and containing about 47% by weight of chemically bound chlorine.


8. A premix composition according to any preceding Claim, characterized in that it comprises by weight:

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halogenated polyether polyol	100
chlorofluorocarbon blowing agent	45
dimethylethanolamine	3.5
condensation product	2 to 4

9. A premix composition according to Claim 8, characterized in that it further comprises 20 parts, by weight, of an amino polyol for reducing surface friability of polyurethane foam, said amino polyol having a hydroxyl number of 600 ± 10 and a viscosity of 280 cps at 25°C.
10. A premix composition according to Claim 8 or 9, characterized in that it further comprises a cell-stabilizing siloxane compound.

For the Applicants


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CHARTERED PATENT AGENT
EUROPEAN PATENT ATTORNEY



European Patent
Office

EUROPEAN SEARCH REPORT

0022336

Application number

EP 80 30 2164.1

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>DE - A1 - 2 822 819</u> (OLIN CORP.) * claims 1, 12; page 9, lines 19 to 26; page 14, lines 7 to 17 * --	1,6, 7, 10	C 08 G 18/18 C 08 G 18/50 C 08 L 71/02 C 08 K 5/20 C 08 K 5/17 C 08 K 5/10
A	<u>US - A - 3 980 579</u> (SYROP et al.) * claims 1,11; column 3, lines 32 to 42; column 5, lines 48 to 55 * --	1,6, 7,10	
A	<u>US - A - 3 248 369</u> (WEIDMAN et al.) * claim 1; column 4, lines 3 to 11 * ----	1,3,4	TECHNICAL FIELDS SEARCHED (Int. Cl.) C 08 G 18/00 C 08 K 5/00 C 08 L 71/00 C 08 L 75/00
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document:
Place of search	Date of completion of the search	Examiner	
Berlin	01-10-1980	MARY	